Indian J. Phys. **75A** (5), 535-540 (2001)

IJP
— an international journal

Decay and TL-glow curves of CaS:Er and CaS:Cu phosphors

C S Gupta
College of Health Sciences, Ministry of Health,
P.O Box-12, State of Bahrain
E-mail : gupta7@hotmail.com

Received 1 April 1999, accepted 18 October 2000

Abstract : Phosphorescence decay characteristics of CaS:Er and CaS:Cu are studied at room temperature to gather information about the type of kinetics involved, decay law, the trap distribution, trap depth; and the thermoluminescence studies to determine the role of activators on the trapping states The trap depths calculated using Randall & Wilkins Equation, Curies Formula and also by Urbach Relation for thermoluminescence (TL) found to be in close consonance with that calculated by peeling off the log $I - t$ (decay) curves, justify the validity of the equation $p = S \exp(-E / kT)$, which neglects re-trapping. Results reveal that phosphorescence decay follows the hyperbolic relation $I = I_0 t^b$ and explained on the basis of superposition theory by assuming the kinetics to be monomolecular

Keywords Thermoluminescence, phosphorescence decay, CaS : Er phosphors

PACS No. : 78.55 Hx

1. Introduction

Blokhinsev [1] was the first among the early worker who derived a theoretical time dependence of the decay of phosphorescence from considerations of electron transitions between various energy levels. Phosphorescence is interpreted as a tunneling recombination between holes and electrons, trapped respectively, by cation vacancies (V centers) and unidentified donor centers [2]. The luminescence arises at the recombination of electrons with holes localized on various V- type centers (a center containing a cation vacancy) and possibly, a charge-compensating impurity [3]. Randall and Wilkins [4] have studied the afterglow of alkaline earth sulphide phosphors and formulated a theory of glow curves. This theory has been extensively used by many workers, to find trap distribution in phosphors. In the present work, an attempt has been made to understand the luminescent nature of CaS:Er and CaS:Cu phosphors. Group of traps contribute to phosphorescence may be assigned the value to its maximum *i.e.* 0.69 eV. The phosphorescence decay, thermo-luminescence and also fluorescence studies reveal that there is only one group of traps which can be associated with host lattice defects.

Correspondence address : Dr. C S Gupta, 223, Itwari Ward, Rampura Road, Near Chhatrashal Akhada, Sagar City (M P.), Pin-470 002, India.

Cu-luminescence has drawn attention in the light of the possibility of using it for lasting. Cu-emission has been used in thermo-luminescence dosimetry phosphors. Still the data on luminescence is limited due to difficulties of incorporating it in its luminescent form [5]. Considering the high TL-efficiency, long storage capability, good TL-reproducibility and relative high dose saturation limit of the glass, it is suggested that the copper-activated silica glass material can be used as good γ-ray dosimeter [6].

2. Preparation of phosphors and experimental procedure

Clean high grade transparent pieces of gypsum are taken, finely powdered to the grain size of about 200 μ and purified by nitric acid treatment of A.R. grade. This fine powder is termed as host. Similarly, carbon powder of A. R. grade obtained from Riedal, Germany is also purified, and used for reducing sulphate to sulphide. Both host and carbon are mixed in the ratio of 4:1 and fluxed with sodium thiosulphate taken equal to the weight of carbon. The varying amount of activator, erbium (erbium oxide obtained from Johnson Matthey & Co., Halton Garden, London EC 1) and / or copper (as cupric sulphate from British Drug House Ltd, Poole-England) is added to above mixture and the charge is fired at 900°C for 2 hours. Then it is pulverised, washed with boiling water, dried and crushed to get the phosphor sample,

keeping extreme purity as the main consideration in the preparation.

Such samples were excited by U. V. lamp (UVS-12) made in U.S.A., emitting predominantly 3650 Å. To maintain excitation energy constant, a stabilizer was also used in conjunction with the lamp. The photo-multiplier tube operated at 900 V obtained from a well-stabilized D. C. Power Supply. The output of the photo-multiplier tube was connected to the potentiometric recorder (CARL-ZEISS-JENA), German made). It was found that four minutes excitation was sufficient to excite the phosphor to the saturation value and as such, for each phosphor, exciting light was switched off after 4 minutes and immediately the shutter of the photo-multiplier tube carefully removed while recording the decay. Thus, intensity as a function of time was plotted by the plotter giving decay curves on a German Recorder.

In case of thermo luminescence, the excited phosphors are first allowed to decay out to the low value to a fixed galvanometer reading and then heated above room temperature by constant warming rate. The warming rate is determined from calibration curves. The phosphor glow increases with the rise of temperature to a certain limit and then decreases. Such a change in glow with temperature recorded for TL using the same German automatic recorder.

3. Theory

If the electrons are raised from valence band to the excited states after absorbing light falling on the crystal, the return of these electrons to the valence band results in luminescence emission. According to Randall and Wilkins theory [7], the trap depth E can be calculated by the equation

$$p = S \exp(-E/kT), \tag{1}$$

where S is an attempt to escape frequency (frequency factor) whose value for alkaline earth sulphide phosphors is 10^9 / sec and p is the probability of escape of electrons from traps per second, E is the trap depth, k-the Boltzmann's constant and T-the absolute temperature. The above equation assumes that the electron freed from traps are not re-trapped and S and E are independent of temperature and that the freed electrons undergo radiative transitions rather than non-radiative transitions. In case of single trap level, intensity decays as

$$I_t = I_0 \exp(-pt), \tag{2}$$

where I_t is the phosphorescence intensity at time t and I_0 is the intensity and n_0 is the number of electrons in excited state at cut-off position. This gives an exponential decay.

In case of distribution of trapping levels, phosphorescence is due to superposition of intensities, each varying exponentially with time. However, in most cases of uniform distribution of traps, the phosphorescence intensity I at any time t is given by Randall and Wilkins [4],

$$I = n S T t^{-1} \quad \text{for} \quad S.t >> 1 \tag{3}$$

However, trap distribution is not uniform in most cases. The intensity in such cases is given by

$$I = I_0 . t^{-b} \tag{4}$$

where b is the decay constant.

In this case, log I *vs.* time does not show a linear relationship because of superposition of number of exponential decays. Following Bube [8] and others, Curie [9], the decay curves were analyzed into three exponentials by the method of subtraction (peeling off of decay curves). The trap depth, corresponding to each exponential was evaluated by using eq. (1) and assuming $S = 10^9$ / sec at room temperature. Traps of different depths contribute to the phosphorescence intensity at different times. The degree of linearity is therefore estimated by evaluating correlation coefficient r [10], the values of which are close to unity with a negative sign indicating that the relationship between log I and log t is almost linear. The negative sign implies that the intensity diminishes with time. The sign of b comes out to be negative, hence the observed hyperbolic decay can be represented by the above equation (4). The value of decay constant indicates the rate of decay. Faster is the decay, higher is the value of b and *vice versa*. They are given in Table 1. Such type of P.D.C. can be represented by a Power Law [eq. (4)] as suggested by Randall and Wilkins [7] and the considered hyperbolic decay as the result of superposition of exponentials. The values of E calculated by peeling off of decay curves are tabulated and are termed as slow, middle and fast components (Table 1).

Table 1. Values of trap-depth, correlation coefficient and decay constant calculated from PDC

Samples series	Erbium Er (%)	Copper Cu (%)	Decay constant (-b)	Correl. coef. (-r)	Trap-depth E in eV		
					Slow	Middle	Fast
A 9	5×10^{-4}	NIL	0.29	0.99	0.63	0.60	0.54
A 11	5×10^{-5}	NIL	0.31	0.99	0.69	0.60	0.57
A 12	1×10^{-5}	NIL	0.24	0.99	0.69	0.60	0.56
A 15	5×10^{-7}	NIL	0.42	0.99	0.67	0.60	0.58
A 16	1×10^{-7}	NIL					
A 17	5×10^{-8}	NIL	0.37	1.00	0.67	0.60	0.56
B 1	NIL	1	0.35	0.98	0.62	0.60	0.56
B 2	NIL	5×10^{-1}	0.38	0.98	0.70	0.60	0.57
B 3	NIL	1×10^{-1}	0.53	0.98	0.66	0.60	0.56
B 4	NIL	5×10^{-2}	0.46	0.98	0.67	0.60	0.58
B 5	NIL	1×10^{-2}	0.38	0.99	0.67	0.60	0.57

4. Results and discussion

4.1 Analysis of decay curves :

To study the mode of decay, the after glow intensity as a function of time was recorded for all the phosphors. *I vs t* plots showed hyperbolic rather than exponential nature (Figure 1). Therefore, the possibility of simple exponential decay with a single trap was ruled out. Log *I vs t* plots did not give the expected straight lines. The log *I vs. t* curve was found to be concave upwards. However, a log – log plots of phosphorescence intensity *vs.*

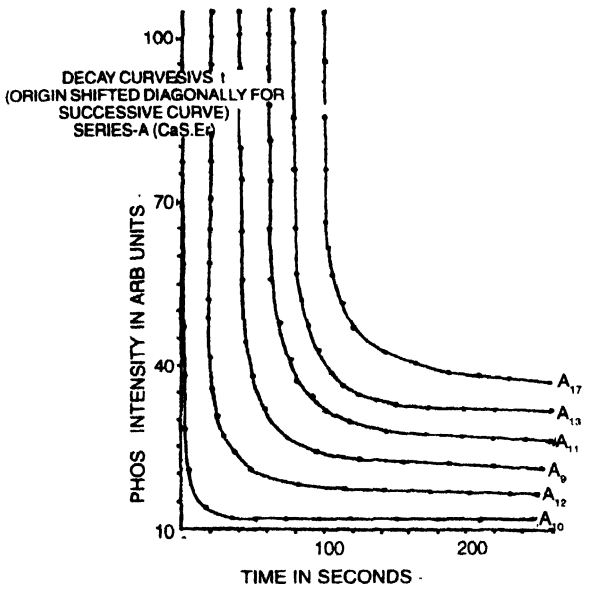

Figure 1. Representative decay curve of CaS:Er phosphors at *RT* (300 K).

time were very nearly straight lines as shown in Figure 2 which helps in concluding that phosphoric decay characteristics in hyperbolic in nature. As the number of exponential distributed

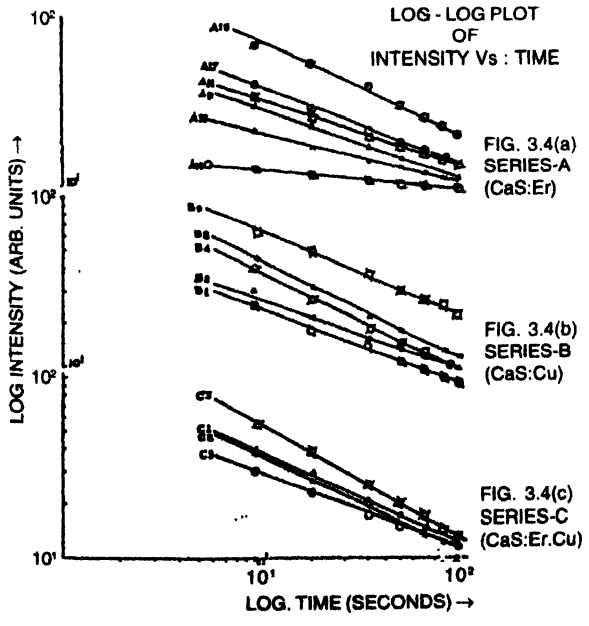

Figure 2. Log *I vs* log *t* plots for CaS:Er phosphors.

traps increases, the decay takes the form of hyperbolic nature due to their superposition. The minimum number of exponentials required to do so can be three as suggested by Bube [8] (Figure 3). The hyperbolic decay is supposed to result from the superposition of intensities, each of which is varying exponentially with time, when different trap depths are involved in contributing to phosphorescence. As the phosphorescence in inorganic phosphors is due to absorption of electrons below conduction band, the thermal energy at room temperature is sufficient to empty the shallow traps which, therefore, become ineffective in phosphorescence decay. The decay measurements at room temperature thus, pertain only to electron traps that are relatively deep.

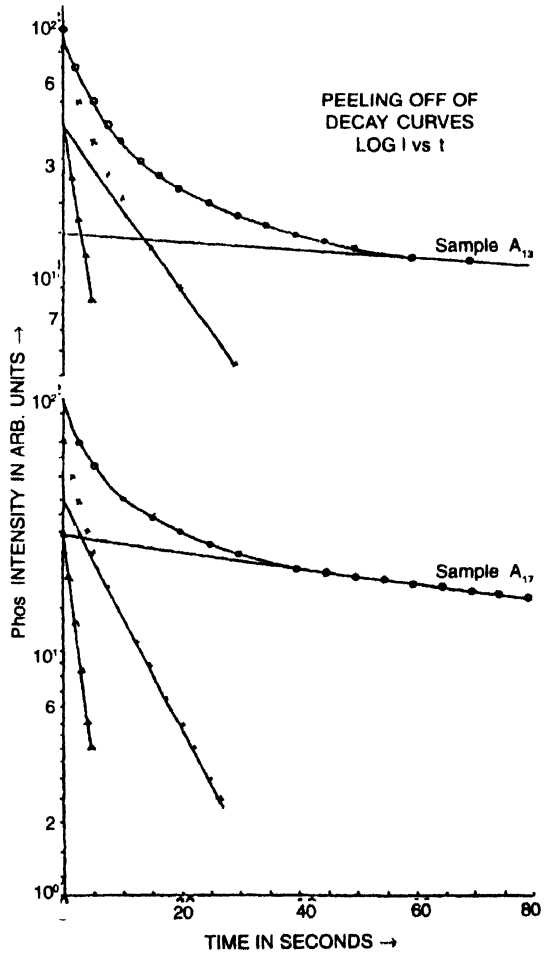

Figure 3. Peeling off of decay curve of CaS.Er phosphors into three components.

First order kinetics is a recombination dominant process. In this process, retrapping is practically negligible in comparison to recombination. This is the process which is frequently observed and widely reported in the literature. In second order kinetics, recombination and re-trapping processes take place with equal probability [11]. The decay is the fastest in first order kinetics. Second order kinetics is found to be more slowly decaying process than the first order kinetics and the third order kinetics decays more slowly than the second order kinetics and

so on. The extent of recombination and re-trapping process decides on the order of kinetics involved. With increasing order of kinetics, the extent of recombination decreases with a simultaneous increase in the extent of re-trapping [11].

A fast component decline in intensity followed by a slower one. The shallow traps decay rapidly, emptying with time, leaving the slower component of deeper traps. The value of decay constant b calculated by the method of least squares [12], is much less than unity. The small variation of decay constant with activator concentration suggests that the activator only modifies the relative importance of the trap but not their mean depth. Hence, the distribution of traps can be assumed to be quasi-uniform. As reported by Garlick and Gibson [13], re-trapping seems to be of no importance in these phosphors. For TL, the formula used by Curie should better be applied. The variation of decay constant with activator concentration, implies proper growth of micro-crystalline powder phosphors. The value of E does not depend on the activator concentration. A slight variation in the trap depths could be due to the perturbation caused by the activators in the distribution of trap densities. The phosphorescence decay, thermoluminescence and fluorescence studies reveal that there is only one group of traps which can be associated with host lattice defects. This is further supported by many other workers that the electron traps are independent of the impurity ions and formed by the crystalline imperfections in the lattice.

4.2 Analysis of TL glow curves :

TL curves for a number of phosphors are plotted as glowing I *vs.* rising T for two warming rates $\beta = 0.62^{\circ}$ K/sec and $\beta = 0.44\ ^{\circ}$K/sec.

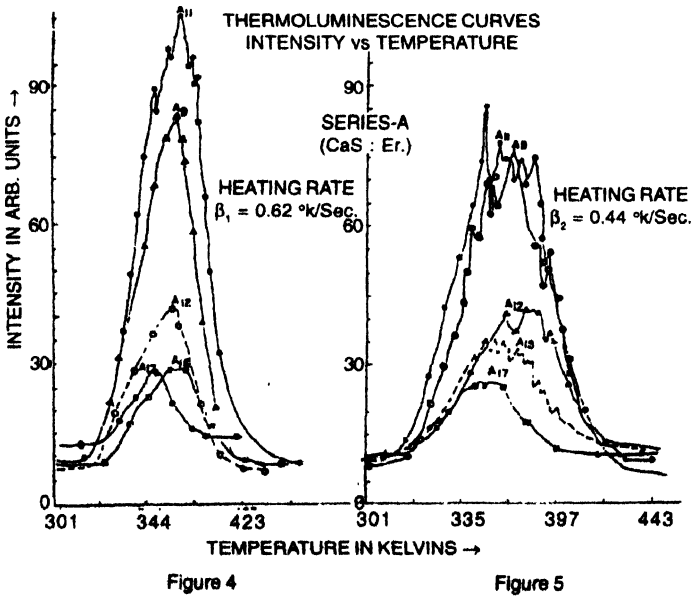

Figure 4. *T vs I* plots of *TL* for CaS:Er. Heating rate : β 1 = 0.62° K/sec.
Figure 5. *T vs I* plots of *TL* for CaS:Er Heating rate : β 2 = 0.44°K/sec.

In our present study of *A*-Series of CaS:Er phosphors, three peaks in the glow curves were observed in all the samples with a large emission intensity. At low heating rate, glow peaks are clearly resolved (Figures 4 and 5). The trapping states of CaS phosphors studied by earlier workers, have reported that either one or two glow peaks maximum, seen during TL of CaS phosphors at room temperature.

In *B*-Series of CaS:Cu phosphors, only one peak is observed (Figure 6 and 7) in all the samples with almost same emission intensity at high as well as low heating rate.

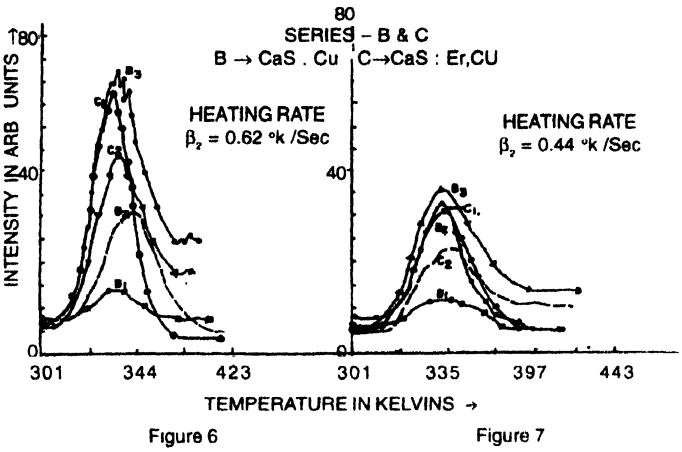

Figure 6. *T vs I* plots of *TL* for CaS:Cu Heating rate β 1 = 0.62°K/sec
Figure 7. *T vs I* plots of *TL* for CaS:Cu Heating rate β 2 = 0.44°K/sec

In all the samples of *A* and *B*-series, the intensity of emission was smaller than that of the peak at the higher temperature.

The glow peak exhibits a first order type of kinetic behaviour The TL intensity decays exponentially. The values of E for all the samples assuming $S = 10^9$ sec^{-1} are calculated by three formulae as below :

Firstly, by Randal and Wilkins [4] Equation : $E(eV) = K T_m (1 + f) \log S$, where $f = [\log (K / T_m^2) / \beta E] / \log S$ is less than unity (= 0.1) can be neglected.

Secondly, by Curies formula [9] : $E(eV) = [T_m(^0K) - T_0(\beta / S)] / [K(\beta / S)]$ where the values of T_0 and K are obtained graphically for various sets of $\theta = \beta / S$ and

Thirdly, by Urbach relation [14] : $E(eV) = T_m / 500$, where T_m is the maximum temperature of glow peak. The values of E are found for each temperature (Table 2).

The increase in glow peak intensity and phosphorescence intensity in the beginning is due to the increase in the number of luminescence centers and the traps with increasing activator concentration. A comparison of glow curves at two different heating rates shows no apparent change in the general shape of the curve, except that the curve as a whole shifts to lower temperature side at the slower heating rate which is in qualitative agreement with theoretical predictions made by many earlier

Table 2. Values of trap-depth from TL-studies as calculated by two heating rates, *viz*; β_1 = 0.62°K/sec. and β_2 = 0.44°K/sec.

Series	β_1 = 0.62°K/sec				β_2 = 0.44°K/sec			Trap-depth E (in eV)								
Sample	T_m Trap-depth				T_{m1}	T_{m2}	T_{m3}	T_{m1}			T_{m2}			T_{m3}		
	E °K	R	C	U	°K	°K	°K	R	C	U	R	C	U	R	C	U
A 9	370	.66	.76	.74	343	353	368	.61	.71	.68	.63	.73	.70	.65	.76	.73
A 11	370	.66	.76.	.74	352	360	368	.62	.73	70	.64	75	72	.65	77	.73
A 12	365	.65	.75	.73	362	375	390	.64	.75	72	.67	.78	75	69	.79	.78
A 15	344	61	.70	.68	341			60	.71	.68						
A 16	365	.65	.75	73	352	357	372	62	.77	.74	63	74	.71	66	.73	70
A 17	350	.62	.72	.70	341	346	357	.60	74	71	.61	72	.69	63	71	.68
B 1	332	.59	.68	66	331			.59	69	66						
B 2	332	.59	.68	66	330			.59	.68	.66						
B 3	331	59	.68	66	330			.59	68	66						
B 4	332	.59	.68	.66	330			.59	.68	.66						
B 5	344	.61	.70	.68	341			.61	.71	.68						

R – Randall & Wilkin's Equation; C - Curie's Formula ; and U – Urbach Relations

workers. It was also observed that the area under the thermo-luminescence curve first increases and then decreases with increase in activator concentration. This indicates an increase in number of traps with concentration in the beginning, as the area under the thermo-luminescence curve is proportional to the number of traps [15]. The reproducible decrease in peak intensity with activator dose may be due to the shift of this glow peak towards lower temperature with dose, which is true for peaks following first order kinetics [16].

The trap depth as a function of activator concentration were plotted. The variation is very little and the nature of variation is very similar to that of Peeling off of decay curves. The trap depth calculated with the help of Curies formula and Urbach relation agree well with the trap depths calculated from the slowest exponential (deeper traps) of the decay curves whereas the trap depths calculated using Randall and Wilkins Equations agree well with the values obtained from the second exponential of the decay curves. This agreement confirms the validity of Randall and Wilkins Equation $p = S \exp(-E/KT)$. Thus, the traps are seen to be associated with defects or to native lattice rather than the activator alone which seems to modify the trap distribution.

The multiple activators used in the fluorescence study give rise to the same emission band at 5750 Å. This would indicate that the emission is due to a native defect in the host crystal such as a cation or anion vacancy. Ivey square low fits the position of the bands with CaS, SrS and BaS. It must be due to sulphur vacancies. Its strong temperature-dependence suggests as an evidence of native defect. Therefore, the observed band at 5750 Å (2.14 eV) may be attributed to sulphur vacancies which may be created during the incorporation of the activators (Er_2O_3 and $CuSO_4$) used with the base material CaS. Hence, it will be reasonable to assume that the blue emissions are characteristics of Cu-activator and the yellow-orange emission may be due to sulphur vacancies [17].

The traps which contribute to the phosphorescence intensity under the present study, have depth in the region of 0.54 to 0.69 eV. This is identical with the values of trap depths determined by earlier workers, irrespective of flux or activators used. Curie [9] also observed that the trap group corresponding to about 0.68 eV is independent of activator concentration. So, it appears that this particular group of traps is characteristics of the host lattice itself.

Acknowledgment

Author is grateful to Ex-Prof J D Ranade, Head, Department of Physics, Saugor University, Sagar (M.P.) and Dr. R. N. Patil, Head, Department of Physics, Shivaji University, Kolhapur (Maharashtra) for providing adequate laboratory facilities to carry out the research work.

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